NAPHTHALENEBORONIC ACIDS

BY

FLAVIUS WEBB WYMAN

B.S., Murray State Teachers College, 1937

M.S., University of Kentucky, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1944

URBANA, ILLINOIS

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INTRODUCTION

From the ease with which benzeneboronic acid undergoes loss of the boronic acid function in hydrolytic and metathetical reactions, it was expected that this group would be displaced in attempted diazonium couplings with hydroxyl- or aminoarylboronic acids. However, Weaver (1) in this laboratory found that the boronic acid group in hydroxy- and dialkylaminobenzeneboronic acids is stable to diazonium salts, and he was able to prepare azo dyes containing boron by means of the coupling reaction. The present work was undertaken to determine whether similar coupling reactions can be effected with hydroxy- and dialkylaminonaphthaleneboronic acids, and to study the chemical properties of these substituted naphthaleneboronic acids and their coupling products. Azo dyes containing the naphthaleneboronic acid group were of particular interest because their availability might make possible a new type of cancer therapy (2,3).

DISCUSSION

Four naphthaleneboronic acids containing dimethylamino or hydroxyl groups have been prepared from the corresponding Grignard reagents and *n*-butyl borate. Some of the chemical properties of these compounds have been studied. In general the naphthaleneboronic acids containing the dimethylamino group appear to be more reactive than those containing the methoxyl group.

The reaction of 4-(N,N-dimethylamino)-1-naphthaleneboronic acid with dilute nitric acid gives 2,4-dinitro-1-(N,N-dimethylamino)-naphthalene. The dinitroamine could not be obtained from dimethyl-α-naphthylamine by reaction with nitric acid under similar conditions. Hot sodium hydroxide solution in the absence of air has very little effect on the aminoboronic acid, but hot sodium hydroxide solution in the presence of air causes hydrolysis of the amino and boronic acid groups and possibly coupling of the naphthalene residues to form a binaphthalene derivative.

4-Methoxy-1-naphthaleneboronic acid is hydrolyzed by refluxing with aqueous acetic acid to yield methyl α-naphthyl ether. 4-(N,N-Dimethylamino)-1-naphthaleneboronic acid reacts with

picric acid in hot 95 per cent ethanol solution to yield the picrate of dimethyl-α-naphthylamine.

4-Methoxy-1-naphthaleneboronic acid reacts with dilute nitric acid to give 2,4-dinitro-1-naphthol, but the product of the reaction of 6-methoxy-2-naphthaleneboronic acid with dilute nitric acid could not be identified.

6-Methoxy-2-naphthaleneboronic acid and 4-methoxy-1-naphthaleneboronic acid do not react with nitrous acid. Also they are only slightly affected by boiling with aqueous sodium hydroxide solution, even in the presence of air.

Coupling reactions with 4-(N,N-dimethylamino)-1-naphthaleneboronic acid result, in most cases, in the loss of the boronic acid group. For instance, coupling with diazotized *p*-aminobenzoic acid yields 4-(N,N-dimethylamino)-1-naphthalene-1-azo-4-carboxybenzene. Coupling with diazotized 3,3′-benzidine-disulfonic acid and 3-benzidine-monosulfonic acid yields dyes which contain boron.

4-Methoxy-1-naphthaleneboronic acid, when treated with certain diazonium salts such as those derived from sulfanilic acid, *p*-aminobenzoic acid, and anthranilic acid, yields substances which contain no boron. However, coupling with diazotized 3,3′-benzidine-disulfonic acid gives a dye which contains boron.

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VITA

The author was born in Lowes, Kentucky, on August 18, 1915. He graduated from the Lowes High School in May, 1935. In the fall of that year he enrolled at Murray State Teachers College, Murray, Kentucky, where he was granted the B.S. degree in June, 1937. He entered the Graduate School of the University of Kentucky in September of 1937 and received the M.S. degree in June, 1939. For the academic year 1939-40 he was Instructor in Chemistry at the University of Kentucky. In the fall of 1940 he entered the Graduate School of the University of Illinois, where he has held a teaching assistantship from 1940 to 1944.